ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PHOTOINDUCED CATIONIC CROSSLINKING OF PEG-BASED POLYMERS WITH HIGHLY REACTIVE VINYL ETHER SIDE CHAINS

M.Sc. THESIS

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Department of Chemistry

Chemistry Programme

JANUARY 2013

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REAKTİF VİNİL ETER YAN ZİNCİRLERİ İÇEREN PEG-BAZLI POLİMERLERİN KATYONİK FOTOPOLİMERİZASYON İLE ÇAPRAZ BAĞLANMASI

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To my family,

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ABBREVIATIONS

VE	**:** Vinyl ether
BAPO	**:** Bis-acyl-phosphine oxide
CQ	**:** Camphorquinone
HBVE	**:** Hydroxy butyl vinyl ether
DMSO	**:** Dimethylsulfoxide

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PHOTOINDUCED CATIONIC CROSSLINKING OF PEG-BASED POLYMERS WITH HIGHLY REACTIVE VINYL ETHER SIDE CHAINS

SUMMARY

Photoinitiated polymerization has gained ascending significance due to its elegant advantages over thermal polymerization. It provides low energy consumption, mild reaction conditions, spatial and temporal control of initiation, eliminates the need for solvents as diluents (i.e. it offers elimination of air and water pollution), rapid curing even at ambient temperature. Photoinitiated polymerization is a considerable industrial process abundantly employed in numerous applications including inks, coatings, varnishes, microelectronics, microlithography, biomaterials, adhesives, dye, advanced technical substrates. Besides, photocurable systems are used to obtain hard and abrasion resistant materials, which are, used as dental fillers, sealants, composite membranes, fiber reinforced plastics. Although the majority of industrial applications of photoinitiated polymerizations for several techniques deal with free radical systems, the corresponding cationic mode is an important industrial process. Photoinitiated cationic polymerization holds considerable promises in the future, especially as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations.

Various cationic photoinitiators such as iodonium, sulfonium, alkoxypyridinium salts exist. Among them, iodonium salts play a vital role in cationic photopolymerization due to their thermal stability, solubility in most of the cationically polymerizable monomers, capability in generating reactive species upon photolysis. The spectral response of diphenyliodonium salts is up to 300 nm. A useful strategy employed for enhancing the performance of these photoinitiators, is the use of activators that absorb light at higher wavelength. The wider spectral sensitivity procured by an activator allows the capture of a higher fraction of the available light emitted from most common UV irradiation. This generates a larger number of initiating species that take part high rate of polymerization of the monomer.

In this thesis, the crosslinking behaviour of PEG-based polymers with highly reactive vinyl ether side chains was investigated upon UV-irradiation in the presence of diphenyliodonium salt. The crosslinking functionality of the polymers was investigated by means of photo-differential scanning calorimetry (Photo-DSC) and real-time infrared (RT-IR) experiments. For comparison, the indirect initiating modes (free radical promoted cationic polymerization and photosensitized cationic polymerization) were also applied.

REAKTİF VİNİL ETER YAN ZİNCİRLERİ İÇEREN PEG-BAZLI POLİMERLERİN KATYONİK FOTOPOLİMERİZASYON İLE ÇAPRAZ BAĞLANMASI

ÖZET

Işıkla başlatılmış polimerizasyon reaksiyonlarına fotopolimerizasyon denir. Genellikle mor ötesi veya görünür bölge ışık kaynakları kullanılır. Fotobaşlatıcının uygun bir dalga boyundaki ışık absorbsiyonu sonucunda oluşan reaktif türler, tek fonksiyonlu monomerlerin polimerizasyonunu sağlarken, çok fonksiyonlu monomerlerin çapraz bağlı yapılara dönüşmesini sağlar.

Fotobaşlatılmış polimerizasyon, pekçok ekonomik ve ekolojik beklentiyi biraraya getirmesiyle, endüstriyel ve akademik çalışmalarda artan bir öneme sahiptir. Fotopolimerizasyon, çeşitli avantajlarından dolayı mürekkepler, kaplamalar, yapıştırıcılar, kontak lensler, vernikler, mikroelektronikler, mikrolitografi, biyomalzemeler vb. gibi pek çok alanda sıklıkla kullanılan önemli bir endüstriyel prosestir. Ayrıca, fotokürlenebilen sistemler, diş dolgu maddeleri, izolasyon maddeleri, kompozit membranlar, fiberle kuvvetlendirilmiş plastikler gibi sert ve aşınmaya karşı dayanıklı malzemelerin eldesinde kullanılmaktadır. Fotopolimerizasyon, oda sıcaklığında yüksek polimerizasyon hızı, düşük enerji tüketimi, çözücüsüz ortamda polimerizasyon, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi gibi avantajlar sağlamaktadır.

Fotopolimerizasyon, termal polimerizasyona göre daha düşük sıcaklıklarda gerçekleştirilebilir. Örneğin; tahta, kağıt, metal ve plastik malzemelerin yüzeylerinin kaplanması ve bu kaplamaların fotokimyasal olarak sertleştirilmesi gibi önemli kullanım alanları sağlayan yöntemler geliştirilmiştir. Lazer ile çalışan video disklerinin üretimi ve diş dolgularının sertleştirilmesi de diğer bir kullanım alanıdır. Bu sistem, çözücüden bağımsız ve ısısal sertleştirmeden sonra yapılan işlemlere gerek duyulmadığından dolayı tehlikesiz olması ve az enerji harcanması açısından, ısısal sertleştirmeye kıyasla daha kullanışlıdır. Buna ek olarak, maksimum çalışma

sıcaklığı düşük olan monomerler sadece düşük sıcaklıklarda polimerleştirilebilir, aksi halde oluşan polimerler depolimerizasyona uğrayarak tekrar monomer formuna gelirler. Ayrıca protein ve enzim gibi ısıya duyarlı biyoyapıların polimerlere bağlanması gibi işlemlerde polimerizasyon düşük sıcaklıklarda gerçekleştirilir. Termal polimerizasyonla karşılaştırıldığında fotopolimerizasyon oda sıcaklığında hızlı, zamansal ve mekan kontrollü olmasından dolayı büyük avantajlara sahiptir. Fakat bu avantajların yanında fotopolimerizasyonla elde edilen polimerlerin molekül ağırlığı, molekül ağırlık dağılımı ve fonksiyonalite gibi özelliklerinin kontrolü mümkün değildir. Bundan dolayı blok ve aşı gibi kopolimerlerin sentezinin fotopolimerizasyonla gerçekleşmesi kısıtlıdır. Başlama mekanizmasının anlaşılması için başlatıcının fotokimyasını bilmek gerekir. Başlatıcıların morötesi ve görünür bölge aralığındaki ışık tarafından, monomerlerin polimerizasyonunu başlatılabilecek serbest radikal veya iyon gibi reaktif tür üretmeleri ve monomerlerin de bu aralıktaki ışık tarafından bozunarak serbest radikal veya iyon vermemeleri gerekir. Monomer sistemlerindeki değişiklerin pahalı olmasından dolayı, fotobaşlatıcıların etkinliğini artırıcı çalışmalar önem kazanmıştır. Özetle bir fotokimyasal polimerizasyon sisteminde en önemli reaktantlar fotobaşlatıcı ve monomerlerdir.

Fotobaşlatılmış polimerizasyonların endüstriyel uygulamalarının çoğunda serbest radikal sistemleri kullanılmasına rağmen, ilgili katyonik mod da önemli bir endüstriyel prosestir. Bütün fotopolimerizasyon prosesleri gibi, katyonik fotopolimerizasyon da enerji tüketimini en aza indirir ve seyreltici olarak kullanılan çözücü ihtiyacını azaltır (örneğin su ve hava kirliliğinin azalmasını sağlar). Ayrıca katyonik fotopolimerizasyon özellikle uçucu maddelerin emisyonunun, toksisitesinin ve moleküler oksijen inhibisyonunun giderilmesinde gelecek için umut vadetmektedir.

Katyonik fotopolimerizasyon da iyodonyum, sülfonyum ve alkoksi pridinyum gibi çeşitli tuzlar, başlatıcı olarak kullanılır. Bunların arasında, onyum tipi fotobaşlatıcılar, fotoliz sonucunda yeterli sayıda reaktif tür oluşturma kapasiteleri, termal olarak kararlı olmaları, katyonik olarak polimerleşen monomerlerdeki iyi çözünürlükleri,elde edilen polimere renk ve koku vermemeleri, başlatıcının ve aydınlatma sonucu oluşan türlerin toksik olmaması, ticari ışık kaynaklarının birçoğunun bu başlatıcının absorbsiyon aralığında ışık yayması gibi özellikleri bakımından önemli role sahiptirler. Ayrıca bu tuzlar katyonik merkezi taşıyan

heteroatomları içerirler. Karşıt iyon olarak genellikle inorganik metal kompleks iyonları kullanılır. Fotoliz sonucunda, katyonik fotopolimerizasyonu başlatan Bronsted asitlerinin yanı sıra serbest radikallerinde oluşmasından dolayı bu tuzlar serbest radikal fotobaşlatıcısı olarak ve eşzamanlı serbest radikal ve katyonik polimerizasyonlarda da kullanılabilmektedir. Katyonik fotopolimerizasyon başlatıcılarının spektral hassasiyetleri,uygun serbest radikal kaynakları ve aromatik uyarıcılar vasıtasıyla yakın UV ve görünür belgeye genişletilmesi mümkündür. Örneğin, difeniliyodonyum tuzları yaklaşık olarak 300 nm dalga boyundaki ışığı absorblamaktadır. Bu durum uzun dalga boyunda ışık kullanıldığında iyodonyum tuzlarının katyonik fotopolimerizasyondaki potansiyel kullanımını kısıtlamaktadır. Bu kısıtlamayı aşmak için difeniliyodonyum tuzu indirek olarak daha yüksek dalgaboylarında absorbsiyon yapan fotobaşlatıcılar veya fotosensitizerler ile parçalanıp katyonik ara yapı oluşturulur. Böylece, daha yüksek dalga boyuna çıkılarak, o dalgaboyu aralığında gerçekleşen polimerizasyonda takip edilir ve daha net ve kesin sonuçlar elde edilir . Ayrıca daha yüksek dalga boyuna çıkılmasıyla, harcanan enerji miktarı da azalır. Bu durum özellikle endüstriyel prosesler için istenen bir özelliktir.

Bu tez çalışmasında, reaktif vinil eter yan zincirleri içeren PEG-Bazlı polimerlerin çapraz bağlanma özellikleri, farklı çözücü sistemleri içinde (dimetilsülfoksit, hidroksi bütil vinil eter) katyonik fotopolimerizasyonla, direk sistem fotobaşlatıcısı difeniliyodonyumheksaflorofosfat tuzu varlığında, UV ışığı ile aydınlatılarak,foto diferansiyel kalorimetrik tarama (Foto-DSC) ve gerçek zamanlı infrared (RT-IR) deneyleri ile araştırılmıştır. Daha yüksek dalga boyunda çalışma imkanı veren ve böylece daha net ve kesin sonuçlar elde etmeye, daha az enerji tüketimi sağlamaya yardımcı olacak, dolaylı başlatıcı sistemleri (serbest radikal desteklenmiş katyonik polimerizasyon ve fotouyarılmış katyonik polimerizasyon) de karşılaştırma yapmak amacıyla uygulanmıştır.

1. INTRODUCTION

Photoiniated cationic polymerization holds considerable promise in an industrial applications because of their crucial advantages as a means of overcoming volatile emissions toxicity and low energy consumption, rapid curing even at ambient temperatures [1]. Photoinitiated cationic polymerization is an important process extensively used in different applications including adhesives, surface coating, inks, dye, varnishes and in the preperation of advanced technical substrates. Photoinitiated polymerization can be initiated by onium salts such as diaryliodonium, alkoxypyridinium with non-nucleophilic anions (e.g. AsF_6^-, SbF_6^-, PF_6^-) due to their thermal stability, solubility in most of the cationically polymerizable monomers and efficiency in generating reactive species upon photolysis [2]. Furthermore, They possess high photolysis quantum yields and are efficient photoinitiators of cationic polymerization when irradiation is carried out using light in the short- to midwavelength UV regions (230-300nm). However, these types of salts to have poor spectral response at high wavelengths. To overcome to this issue, onium salts are used in combination either with photoexcited sensitizers, which are electron donor compounds in the excited charge-transfer complexes, or with free radicals. The more extensive spectral sensitivity procured by these co-initiators provide the capture of superior fraction of the available light emitted from most common UV irridation sources. Photolysis of these salts generates to the formation of reactive cation or Bronsted acids which react with abundantly with monomers such as vinyl ethers and cyclic ethers [3].

Vinyl ethers (VE) are very reactive monomers that undergo a rapid cationic polymerization in the presence of photogenerated protonic acids. One of the divergent feature of cationic UV-curing is that the chain reaction continues toproceed even in the dark, thereby achieving a more decisive deep-through cure of the sample. These low-odor and non-irritating monomers are now commercially existent, thus allowing a fine tuning the UV-curable formulation in order to attain the desired features of the polymer material for the industrial applications. UV-curable VE

monomers are anticipated to find their main industrial applications such as fast-drying coatings, quick-setting adhesives and sealants, and negative photoresists in the graphic arts and microelectronics.

The objective of this work is to present the crosslinking features of PEG-based polymers with highly reactive vinylether side chains in the presence of different solvents (dimethyl sulfoxide, hydroxybutyl vinylether) in photoinduced cationic polymerization with diphenyliodonium hexafluorophosphate salt. Furthermore, to point out differences as well as parallels between the initiators for direct and indirect action(free radical promoted cationic polymerization, photosensitized cationic polymerization). Special highlight will be denoted on the use of long wavelength free radical photoinitiator and photosensitizer such as bis-acyl-phosphine oxide (BAPO) and camphorquinone, respectively.

2. THEORETICAL PART

2.1 Photopolymerization

Photopolymerization has gained increasing interest due to its excellent advantages in comparsion to thermal polymerization. Photoiniated cationic polymerization holds considerable promise in an industrial applications because of their crucial advantages as a means of overcoming volatile emissions toxicity and low energy consumption, rapid curing even at ambient temperatures It provides high rate of curing even at ambient temperature, low curing temperature, low energy input, temporal and spatial control of the polymerization, solvent free formulations, thence elimination of air and water pollution [4]. Furthermore, it procures chemical utility since a wide range of polymers can be polymerized photochemically.

These unique advantages have been exploited in a diversity of applications including coatings, adhesives, inks, varnishes, biomaterials, fabrication of printed circuit boards, printing plates, replication of optical disk optical waveguides, microelectronics, microlithography.

Some other less traditional but interesting applications such as production of laser videodiscs and fabrication of 3D objects are available [5]. Moreover, photocurable systems are used to obtain hard and abrasion resistant materials which are used as acrylate dental fillers, sealants, composite membranes and fiber reinforced plastics [6].

Increasing relevance continues in identifying the reactive species involved in the polymerization process by laser flash photolysis, time-resolved fluorescence and phosphorescence and electron spin resonance spectroscopy as well as monitoring the polymerization itself by means of real time IR spectroscopy, in-line NIR reflection spectroscopy, differential scanning calorimetry, in situ dielectric analysis, and recently developed optical pyrometry.

Photopolymerization is considered as a process that converts a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions),

which are generated from light-induced reactions by photosensitive compounds, namely photoinitiators and/or photosensitizers, by ultra violet-visible (UV-Vis) light irradiation [7]. The wavelength or range of wavelengths of the initiating source is determined by the reactive system including the monomer(s), the initiator(s), and any photosensitizers, pigments or dyes which may be present. An active center is produced when the initiator absorbs light and undergoes some type of decomposition, hydrogen abstraction, or electron transfer reaction.

Only difference between the conventional thermal polymerizations with photopolymerizations is up to generation of active centers, the rest of the process of photopolymerizations (propagation and termination) is in the same manner with traditional (i.e. thermal) polymerizations.

In fact, photopolymerization can be subdivided into three categories: radically, cationically and anionically, much effort has been devoted to free radical and cationic systems mainly due to the availability of a wide range of photoinitiators and the great reactivity of monomers.

Although the majority of industrial applications of photoinitiated polymerizations for various techniques deal with free radical systems, the corresponding cationic mode is an important industrial process.

Like all photopolymerization processes, photoinitiated cationic polymerization minimizes energy consumption, and eliminates the need for solvents as diluents (i.e. it offers elimination of air and water pollution). Moreover, once initiated, cationically polymerizable monomers undergo dark-polymerization in which they slowly polymerize without radiation. Furthermore, photoinitiated cationic polymerization holds considerable promises in the future, particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations [8].

2.1.1. Free Radical Polymerization

Free radical photopolymerization plays a predominant role in a variety of applications due to its coherence to a wide range of formulations such as acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV or visible range. Photo-induced free-radical polymerization comprises four basic steps.

Firstly, *Photoinitiation step* can be considered as generation of radicals as a result of absorption of incident light by photoinitiators and following reaction of occuring radical and monomer.

Secondly, *Propagation step* involves repeated addition of monomer units to the chain radical produces the polymer backbone.

Thirdly, *Chain transfer step* is a term of termination of growing chains whereby hydrogen abstraction from various species (e.g., from solvent) and formation of new radicals capable of initiating other chain reactions.

Lastly, *Termination step*, involves termination of chain radicals by disproportionation or recombination reactions.

Only difference between the conventional thermal polymerizations with photopolymerizations is up to generation of active centers, the rest of the process of photopolymerizations (propagation, transfer and termination) is in the same manner with traditional (i.e. thermal) polymerizations.

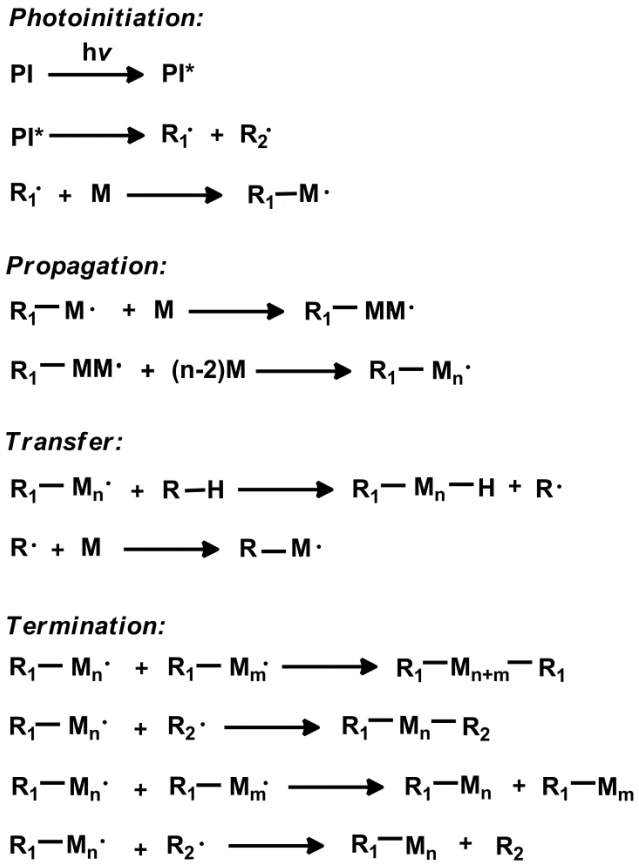

Figure 2.1 Basic reactions in free radical photopolymerization.

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In photo-induced free-radical polymerization, photoinitiators are sub-divided into two categories including *Type I* and Type *II* in respect of the process by which initiating radicals are formed. They possess high photolysis quantum yields and are efficient photoinitiators of cationic polymerization when irradiation is carried out using light in the short- to midwavelength UV regions (230-300nm). However, these types of salts to have poor spectral response at high wavelengths. To overcome to this issue, onium salts are used in combination either with photoexcited sensitizers, which are electron donor compounds in the excited charge-transfer complexes.

2.1.1.1. Type 1 photoinitiators (Unimolecular photoinitiator systems)

Photoinitiators termed unimolecular are so designated because the initiation system involves only one molecular species interacting with the light and producing free-radical active centers. These substances undergo a homolytic bond cleavage upon absorption of light (eq. 2.1). The fragmentation that proceeds to the formation of radicals is, in consideration of chemical kinetics, a unimolecular reaction (eq. 2.2).

$$PI \xrightarrow{h\nu} PI^* \xrightarrow{k} R_1\cdot + R_2\cdot \qquad \textbf{(2.1)}$$

$$\frac{d[R_1^\cdot]}{dt} = \frac{d[R_2^\cdot]}{dt} = k[PI^*] \qquad \textbf{(2.2)}$$

The number of initiating radicals comprised upon absorption of one photon is termed as quantum yield of radical formation ($\phi_{R\cdot}$) (eq. 2.3).

$$\Phi_{R\cdot} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \qquad \textbf{(2.3)}$$

Hypothetically, cleavage type photoinitiators should have a $\phi_{R\cdot}$ value of two since two radicals are formed by the photochemical reaction. The values observed, however, are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or non-radiative decay and energy transfer from the excited

state to other, ground state molecules, a process referred to as quenching. The reactivity of photogenerated radicals with polymerizable monomers is also to be taken into consideration. In most initiating systems, only one in two radicals formed adds to monomer thereby initiating polymerization. The other radical usually undergoes either combination or disproportionation. The initiation efficiency of photogenerated radicals (f_P) can be calculated by the following formula:

$$f_P = \frac{\text{Number of chain radicals formed}}{\text{Number of primary radicals formed}} \qquad \textbf{(2.4)}$$

The overall photoinitiation efficiency is expressed by the quantum yield of photoinitiation (ϕ_P) according to the following equation:

$$\Phi_P = \Phi_R . x\ f_P \qquad \textbf{(2.5)}$$

Regarding the energy neccessity, it has to be said that the excitation energy of the photoinitiator has to be higher than the dissociation energy of the bond to be ruptured. The bond dissociation energy, on the other hand, has to be high enough in order to ensure long term storage stability.

Initiating radicals, formed by direct photofragmentation process (α or less common β cleavage) of *Type I* photoinitiators upon absorption of light, are capable of triggering polymerization. As illustrated in Figure 2.2, the photoinitiator forms an excited singlet state, which then undergoes rapid intersystem crossing to form a triplet state. In the triplet state, two radicals (benzoyl and benzyl radicals) are generated by α-cleavage fragmentation. Most probably, polymerizaton proceeds upon the benzoyl radical which is the major initiating species, while, in some other instances, the benzyl radical may also contribute to the photoinitiation.

The role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes; they are not affected by light.

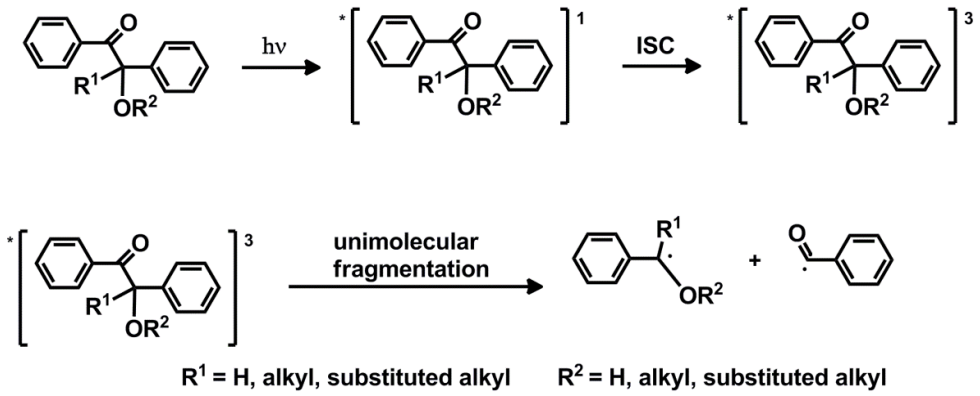
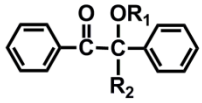
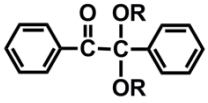
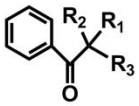
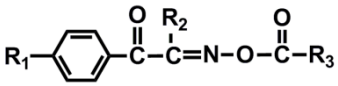
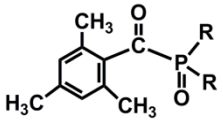


Figure 2.2 Generation of initiating radicals from decomposition of a Type1 photoinitiator.

Table 2.1 Structures of typical Type I radical photoinitiators

Photoinitiators	**Structure**	**λ_{max} (nm)**
Benzoin ethers	 R_1 =H, alkyl R_2 =H, substituted alkyl	323
Benzil ketals	 R =CH_3, C_3H_7, CH_2	365
Acetophenones	 R_1 = OCH_3, OC_2H_5 R_2 = OCH_3,H R_3 = C_6H_5,OH	340
Benzyl oximes	 R_1=H, SC_6H_5 R_2= CH_3,C_6H_{13} R_3= C_6H_5, OC_2H_5	335
Acylphosphine Oxides	 R= C_6H_5, OCH_3	380

2.1.1.2 Type II photoinitiators (Bimolecular photoinitiator systems)

In order to form the propagating radical, in this mode, two molecular species are needed, a photoinitiator that absorbs the light and co-initiator that acts as a hydrogen or electron donor, respectively. Because of that, this mode is termed as bimolecular photoinitiators. Owing to their excitation energy is lower than the bond dissociation energy, these photoinitiators can not undergo *Type I* reactions. The excited molecule can, however, react with another component of the polymerization mixture (co-initiator (COI)) to produce initiating radicals (eq. 2.6). In this case, radical generation follows second-order kinetics (eq. 2.7).

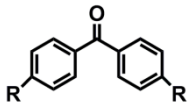
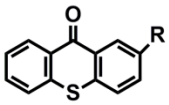
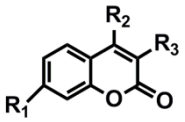
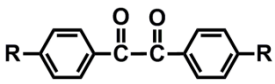
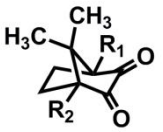
$$PI \xrightarrow{h\nu} PI^* + COI \xrightarrow{k} R_1\cdot + R_2\cdot \qquad \textbf{(2.6)}$$

$$\frac{d[R_1^\cdot]}{dt} = \frac{d[R_2^\cdot]}{dt} = k[PI^*][COI] \qquad \textbf{(2.7)}$$

In the one hand, Classic Type II photoinitiators involve aromatic carbonyls such as benzophenone and derivatives [9-12], thioxanthone and derivatives [13-16], benzyl, quinines, and organic dyes[17-21], on the other hand, alcohols, ethers, amines, and thiols are used as hydrogen donors. Recently, thiol and carboxylic acid derivatives of thioxanthones have been reported to initiate photopolymerization without co-initiators as they contain functional groups with H-donating nature [22-24]. Photopolymerization is considered as a process that converts a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated from light-induced reactions by photosensitive compounds, namely photoinitiators and/or photosensitizers, by ultra violet-visible (UV-Vis) light irradiation.

In this mode, free radical active centers are produced by hydrogen abstraction or photo-induced electron transfer process.

Table 2.2 Structures of typical Type II photoinitiators.

Photoinitiator	Structure	λ_{max} (nm)
Benzophenones	 R = H, OH, $N(C_2H_5)_2$, C_6H_5	335
Thioxanthones	 R = H, Cl, isopropyl	390
Coumarins	 R_1 = $N(C_2H_5)_2$, $N(CH_3)_2$ R_2 = CH_3,eyelopentane R_3 = benzothiazole, H	370
Benzils	 R = H, CH_3	340
Camphorquinones	 R_1 = CH_3, H R_2 = H, CH_3	470

Hydrogen abstraction

Bimolecular hydrogen abstraction is restricted to diaryl ketones [25]. The free radical generation process is the H-abstraction reaction of triplet photoinitiator from hydrogen donors (R-H) such as amines and alcohols. The radical derived from the donor can initiate the polymerization, whereas ketyl radicals stemming from aromatic carbonyl compound are usually not reactive toward vinyl monomers because of bulkiness, the delocalization of the unpaired electrons, or both.

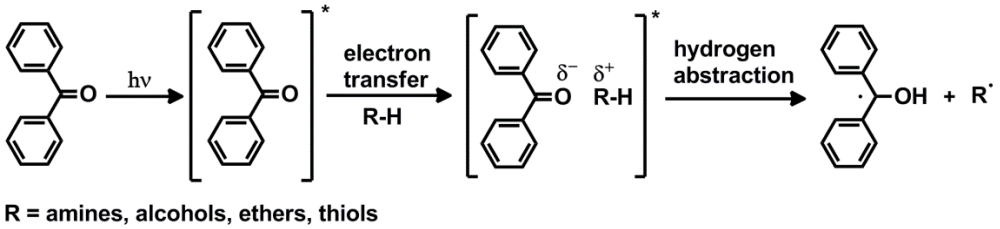
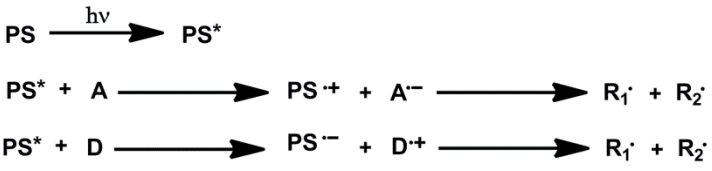


Figure 2.3 Formation of initiating radicals from photolysis of Type II photoinitiator in the presence of suitable hydrogen donor.

Photoinduced electron transfer reactions and subsequent fragmentation

Photoinduced electron transfer is a more general process, which is not limited to a certain class of compounds and is more important as an initiation reaction comprising the majority of bimolecular photoinitiating systems. The photoexcited compounds (sensitizer) can act as either an electron donor with the coinitiator as an electron acceptor or vice-versa. The radical ions obtained after the photoinduced electron transfer can generally undergo fragmentation to yield initiating radicals (eq. 2.14-2.16).

The electron transfer is thermodynamically allowed, if Gibbs Energy Change (ΔG) calculated by the Rehm-Weller equation (eq. 2.17) is negative [26].



(2.8)

(2.9)

(2.10)

$$\Delta G = F\,[E_{1/2}^{ox}(D/D^{+}\cdot) - E_{1/2}^{red}(A/A^{-}\cdot)] - E_S + \Delta E_c \qquad \textbf{(2.11)}$$

where
F = Faraday constant
$E_{1/2}^{ox}(D/D^{+}\cdot)$, $E_{1/2}^{red}(A/A^{-}\cdot)$ = redox potentials of the donor and acceptor
E_S = excitation state of the reactive state of the sensitizer; $E_S = h\nu$
ΔG = Coulombic stabilization energy

2.1.2. Cationic photopolymerization

Even though lots of industrial applications are based on the free radical photopolymerization due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers, there are some drawbacks associated with this type of polymerization including the inhibition effect of oxygen and post-cure limitations.However, the corresponding cationic mode is a valuble industrial technic due particularly to provide solution to this issues [27,28]. Moreover, first initiated, cationically monomers including vinyl ethers and epoxides undergo dark-

polymerization in the absence of light. There are two ways for the initiation of photoinduced cationic polymerization; direct photolysis and indirect photolysis.

2.1.2.1. Direct systems for cationic photopolymerization

Onium salt photoinitiators generate initiating species upon irradiation at appropriate wavelengths. Their synthesis and initiation mechanism is one of the most important research area for polymer science The mechanism usually refered to as direct photoinitiation [29]. The cationic polymerization of suitable monomers is initiated by both radical cation and/or protonic acid that are generated photochemically upon photolysis of cationic photoinitiators. Most photoinitiators, used in cationic photopolymerization mainly absorbs light between 225 to 350 nm. For practical applications, however, they are expected to absorb light at quite longer wavelengths in order to rise the accuracy of the yield of polymerization and decrease the consumption of the energy. Several attempts have been described to overcome this problem. Three modes of indirect initiation are possible depending on the role played by the additives in the initiation of the polymerization as it will described in the following parts. General scheme direct sysyems for photo-induced cationic polymerization is depicted in Scheme 2.4. A photo-sensitive compound, namely photoinitiator (PI), absorbs incident light and undergoes decomposition leading to production of initiating species. Active species, namely a radical cation ($R^{+\bullet}$) in turn, react with cationic polymerizable monomers (M), and yield polymer.

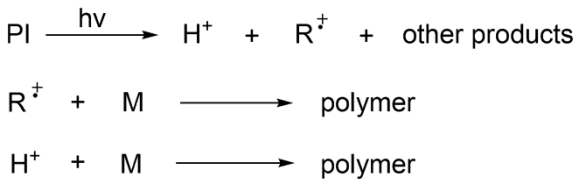


Figure 2.4 General scheme of photo-initiated cationic polymerization.

Onium salts

Onium salts are the most widely used cationic photoinitiators. They contain chromophopric groups as the light sensitive body with heteroatoms as cationic centers in the structure. As counterions, mostly inorganic metal complex anions are used [30]. In recent years, onium salts with highly nucleophilic counterions such as

Cl^-, Br^- and I^- have also been used in conjuction with Lewis acids [31-33]. The most frequently used onium salts are aryldiazonium, diaryl iodonium, triarylsulfonium and tetra alkyl phosphonium salts with non-nucleophillic counter ion.

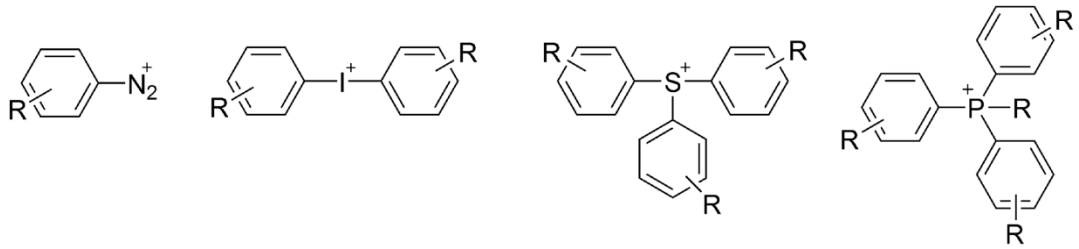


Figure 2.5 Molecular structures of mostly used onium salt photoinitiators

Aryldiazonium salts

Being easily obtained starting from the aniline derivates, these salts produce Lewis acids upon irradiation which can initiate polymerization itself or react with a hydrogen donor compound in the reaction mixture to yield Brønsted acid which is capable of initiating appropriate monomers.

Although these salts have high quantum yields changing in the range 0.3 and 0.6, their practical applications are quite impossible owing to their lack of thermal stability and evolution of nitrogen gas during the process.

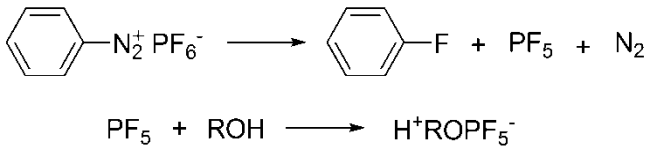


Figure 2.6 Photoinitiating mechanism of aryldiazonium salts.

Diaryliodonium salts

As diphenyliodonium hexafluorophosphate has used as a direct mode cationic photoinitiator in this thesis, diaryliodonium salts are the most frequently used halonium salts because they are easy to obtain and highly reactive [34-36]. The nucleophillic halogen counter-ion must be replaced by a non-nucleophillic anion in order to prevent the termination of cationic polymerization.

Because of their poor spectral sensitivity, either an electrophillic substitution reaction can be applied on the aromatic rings to posses electron donating species which can move absorption bands to lower energies or some special additives can be used to carry out polymerization at longer wavelengths.

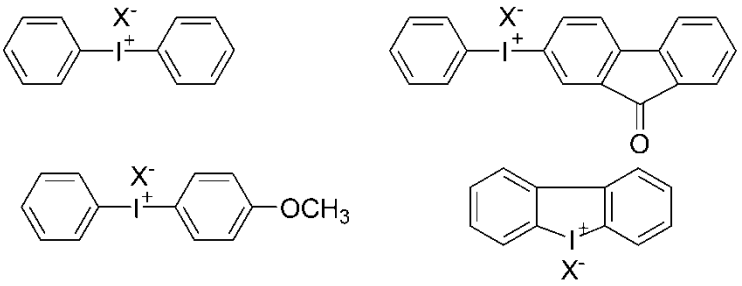


Figure 2.7 Molecular structures of mostly used diaryl iodonium photoinitiators.

Photolysis of diaryliodonium salts take place either through homolytic or heterolytic cleavage of the halogen-aryl bond to form species which react with a hydrogen donor compound to yield a Brønsted acid that initiates polymerization (Figure 2.8).

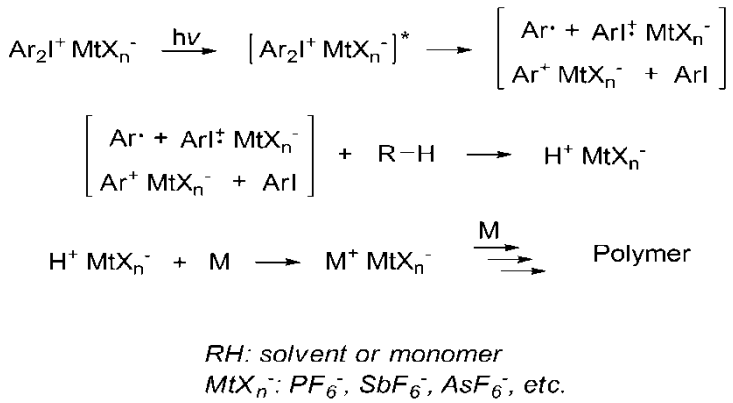


Figure 2.8 Photo-initiated polymerization by irradiation of $Ph_2I^+PF_6^-$.

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Notably, the electron donating subtituents on the aromatic structures not only shifts absorption bands to longer wavelengths, but also favors photolysis of diaryliodonium salts to afford higher polymerization rates.

Sulphonium salts

Widely used sulphonium salts for cationic polymerizations are depicted in Figure 2.9 [37-39].

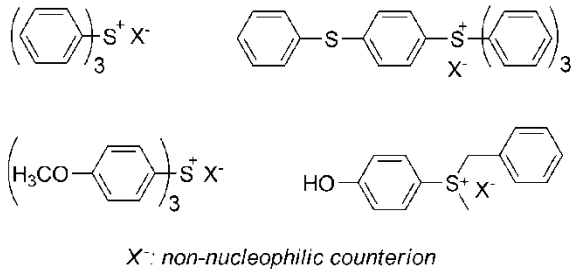


Figure 2.9 Common sulphonium salts.

When they are subjected to appropriate wavelengths, triaryl sulphonium salts (TPS) undergo either a homolytic or a heterolytic cleavage followed by a proton release after some additional steps which are summarized in (Figure2.10).

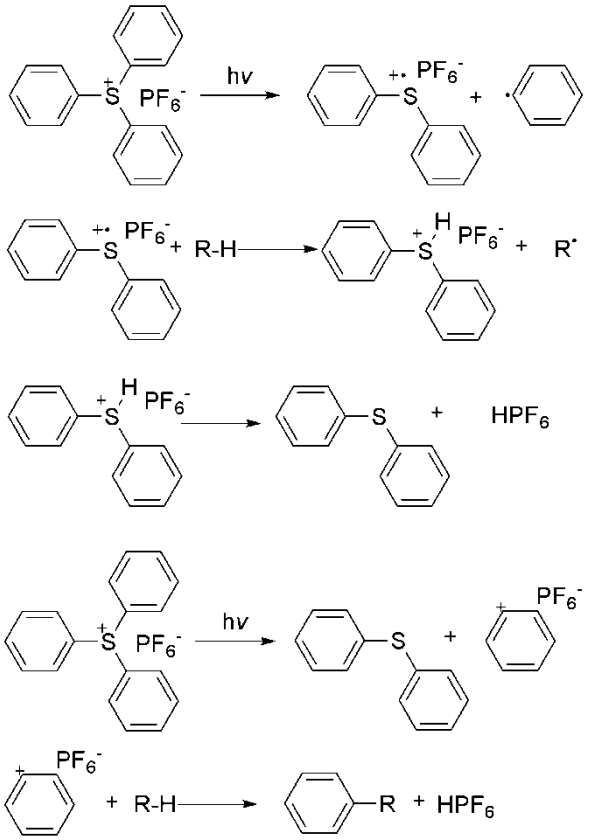
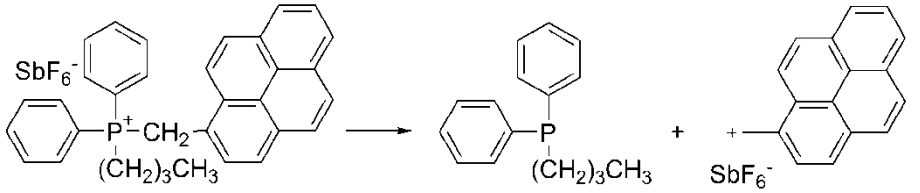


Figure 2.10 Photochemically generation of protons from triaryl sulphonium hexafluorophosphate.

Phosphonium salts

After the photolysis of benzyl or pyrenylmethyl groups containing phosphonium salts, carbon centered cations are produced through a heterolytic bond rupture according to equation 2.12. These cations are accepted to be the initiating species in cationic photopolymerization due to their highly stability [40].



(2.12)

N-Alkoxy pyridinium salts

N-Alkoxy Pyridinium salts are obtained with relatively high yields by a reaction of pyridine *N*-oxides with a triethyloxonium salt in methylene chloride or chloroform. Quinolinium salts can also be prepared from the corresponding *N*-oxides.[41] In both cases, an anion exchange is not necessary since the triethyl oxonium salt is available with non-nucleophilic counter anions. The most frequently used photoinitiators of this type are depicted in Figure 2.11. The spectral response of these salts is range from 260 to 310 nm.[42]

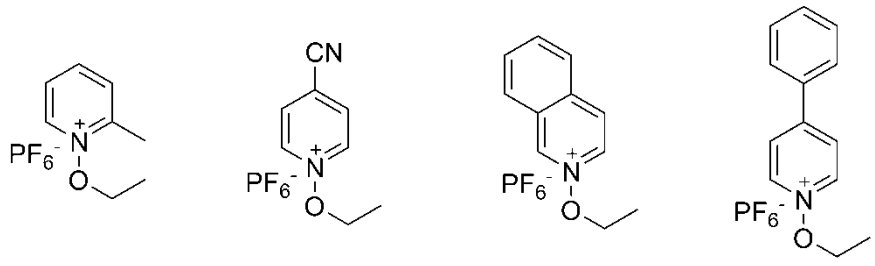


Figure 2.11 Commonly used *N*-alkoxy pyridinium salts.

The photopolymerization of appropriate monomers including vinyl ethers and and epoxides can be initiated in the presence of N-Alkoxy pyridinium salts such as N-ethoxy–2-methylpyridinium hexafluorophosphate (EMP^+ PF_6^-). The mechanism is shown in Figure 2.12.

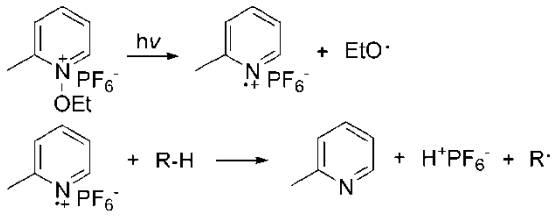


Figure 2.12 Generation of protonic acid during photo-induced decomposition of $EMP^+ PF_6^-$.

Phenacyl salts

Although phenacyl sulfonium salts are easily obtained and highly preferable due to their thermal stabilility and higly phoresponsivity, their poor solubility in common monomers makes them unpreferable [43]. To overcome this limitation, phenacyl sulfonium salts are treated with alkyl substituents. The chemical structures of the salts having good solubility can be seen in Figure 2.13.

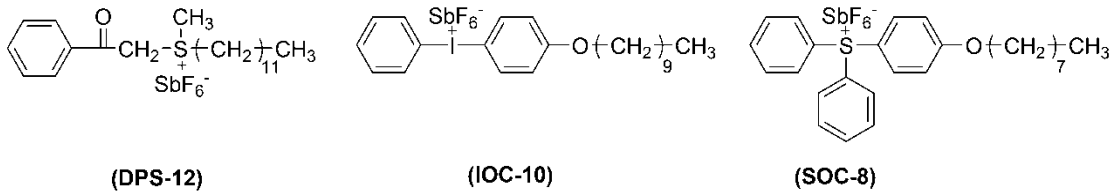


Figure 2.13 Chemical structure of phenacyl sulfonium salts.

The photolysis of phenacylammonium salts are irreversible and different than their sulfonium analogs. Their behaviour of high light absorbtion range from 300 to 350 nm makes them preferable for cationic photopolymerization in appropriate monomers including vinyl ethers and epoxides.[44]

2.1.2.2 Indirect systems for cationic photopolymerization

Photochemical processes occur with absorption of the incident photon energy. Medium- and high-pressure mercury lamps that are frequently used as light sources provide emissions at 313 and 366 nm. If daylight is to be used for curing a coating formula, light absorption at wavelengths longer than 400 nm is highly desired. Although electron-donating substituents can attached to the structure as mentioned before, some electron-rich compounds such as trimethoxybenzene or

hexamethylbenzene can be added to polymerization mixture to form charge transfer complexes (CTCs) with initiators in the electronic ground state that have absorptions at longer wavelengths. Furthermore, some special additives can be used in collabration with photoinitiators to observe the photopolymerization at longer wavelengths. Especially, the light absorbing species are preferable as addivitives here. Provided the systems thus obtained do initiate cationic polymerizations. Initiation methods do not involve the electronic excitation of the onium salt. The initiation mechanisms are entirely different from that found for direct photolysis of onium salts. The initiation can be explained through one of the following mechanisms:

Sensitization by Classical Energy Transfer

This mechanism involves the electronic excitation of the ground state of the sensitizer, a molecule possessing a suitable absorption spectrum, to its excited state. Energy may be transferred from the excited sensitizer (S*) to the onium salt (I) by either resonance excitation or exchange energy transfer (Figure 2.14.). Depending on the two components involved, the energy transfer may proceed either in the excited singlet or in the triplet state.

$$S \longrightarrow S^*$$

$$S^* + I \longrightarrow S + I^*$$

Figure 2.14 Sensitization mechanism by classical energy transfer.

In consequence of the transfer process, the sensitizer returns to its ground state and excited onium salt species (I*) are formed. The further reactions may also differ from those, taking place when the onium salt is excited by direct absorption of light. This conclusion has been drawn on the bases of product analyses [45-47]. An obvious explanation for this difference is the spin multiplicity: in the below discussed sensitized excitations triplet states of the onium salts are populated. In contrast to this, through direct irradiation of the onium salt, electrons are excited primary to the singlet state. A sufficient energy transfer requires the excitation energy of the sensitizer E*(S) to be at least as large as the excitation energy of the photoinitiator E*(I). The photopolymerization with most onium salts can be sensitized by commonly used photosensitizers, such as acetophenone or naphthalene. However, in

many cases this reaction does not proceed via energy transfer, since most onium salts are capable of oxidizing these sensitizers in an exciplex formed between sensitizer and onium salt. Diphenyl iodonium salts are shown to take action of energy transfer with suitable additives like m-trifluoromethyl acetophenone [48]. However, energy transfer using TPS salts are shown to be impossible because of unfavorable thermodynamic conditions. Energy transfer sensitization did not turn out to be technically useful, although being a possible pathway in starting the decomposition of onium salts. The reason is that the high triplet energies required allow only the use of sensitizers absorbing at wavelengths below 350 nm. Other multicomponent initiating systems show a more practical spectral response.

Free radical promoted cationic polymerization

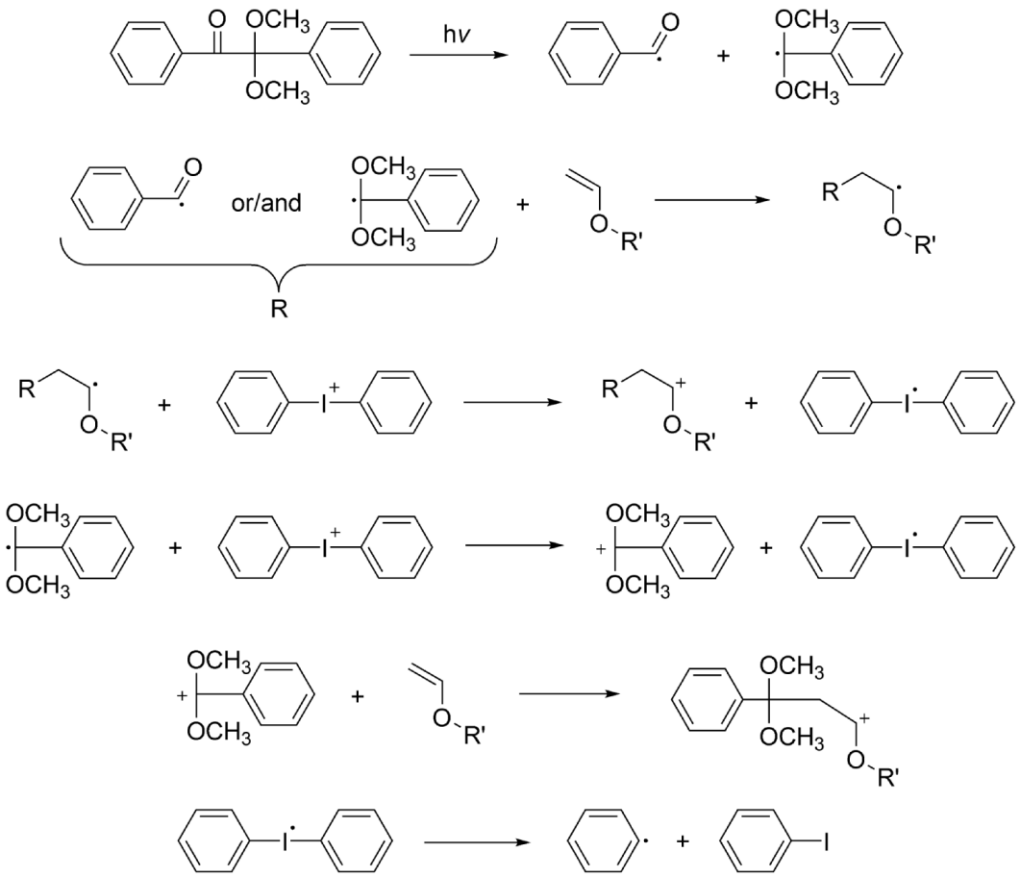


Figure 2.15 Typical free radical promoted cationic polymerization.

Onium salts can oxidize the majority of free radicals to form cations that are considered as initiating species for cationic photopolymerization as can be seen from the following mechanism in Figure 2.15 [49-51].

While, vinyl ether(VE) type monomers raect with the radical ($R\cdot$) generated photochemically from photoinitiator (PI) and give rises a new radical ($R\text{-}M\cdot$) which is also oxidized by the diaryliodonium salt, cyclic monomers such as cyclohexeneoxide do not undergo such oxidation process. In the one hand, photopolymerization of cyclic monomers is initiated by only primary radicals, on the other hand, polymerization of VE monomers is initiated by both primary and secondary radicals.

This technic is usually termed as the free radical promoted cationic polymerization. This so-called free radical promoted cationic polymerization is an excellent and fairly flexible type of indirect initiation of cationic polymerization.

Sensitization via exciplexes

Photosensitizers provide the high rate of polymerization and requires less energy consumption [52]. Because of these functionalities of photosensitizers,they collaborate with photoinitiators in order to accelarate the rate of reaction. In order to form initiating species for cationic photopolymerization, electron-rich polyaromatic compounds such as anthracene, pyrene, and perylene [53] are proper as photosensitizers as they give redox reactions with DPI salts through exciplex. The reaction mechanism is shown in Figure 2.16.

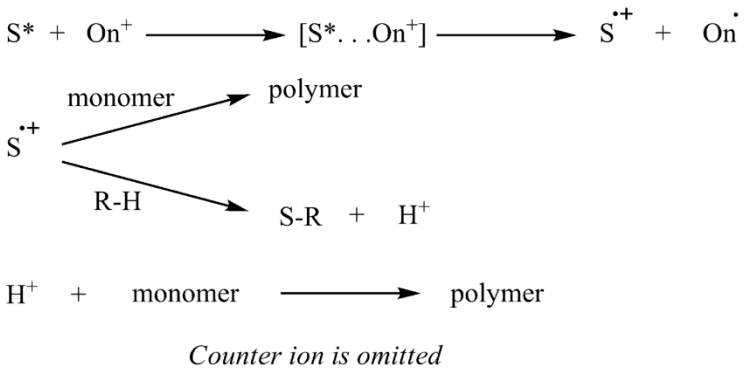


Figure2.16 Mechanism of a polymerization followed via exciplex formation through the excited sensitizer with the ground state onium salt.

On the other hand, since their poor solubility in many monomers and toxicity, these sensitizers should be functionalized through some ways. One way to obtain non-toxic polymers through sensitization is to copolymerize compounds which can behave either as a photosensitizer and monomer with different monomers. Another way is to polymerize these monomeric photosensitizers and afterwards subject them to sensitize the polymerization of convenient monomers. In both ways non-toxic and odorless polymers can be obtained after polymerization.Some of functionalized polyaromatic sensitizers can be seen from Figure 2.17.

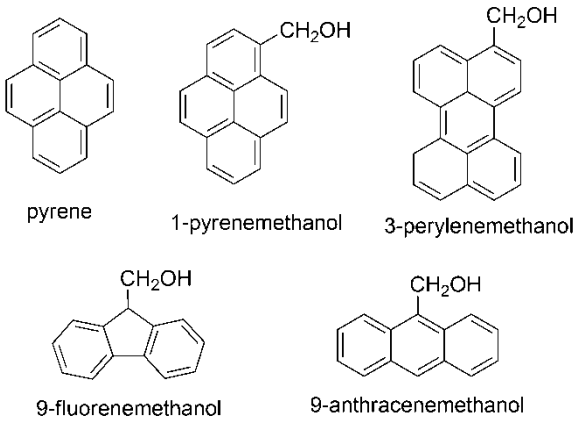


Figure 2.17 Functionalized polyaromatic sensitizers.

Ground state CTCs

Even though there are some doubts about this method, some salts can carry on to polymerization upon irradiation.

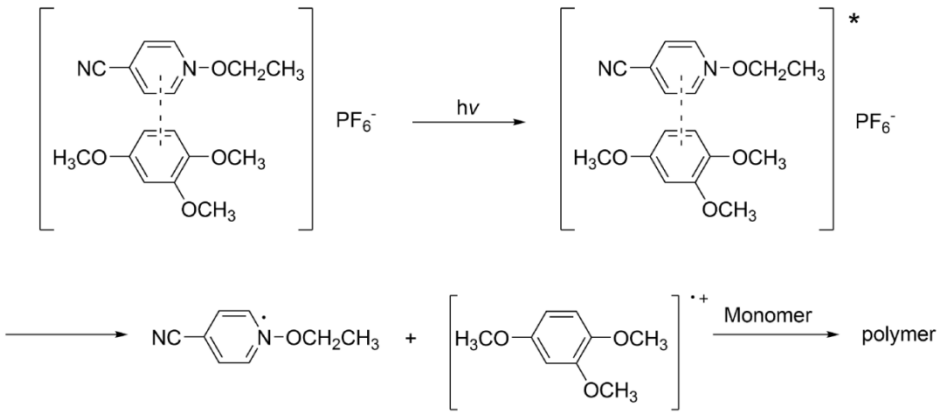


Figure 2.18 Photoinitiation by CTCs.

For instance, pyridinium salts with electron donors including methyl and methoxy substituted benzene are suitable of forming ground state CTC.[54] These occured complexes absorb light at higher wavelengths, where the components are virtually transparent. To give a specific example, complex formed between *N*-ethoxy-4-cyano pyridinium hexafluorophosphate and 1,2, 4-trimethoxybenzene possesses an absorption maximum at 420nm.

2.2. Vinyl Ethers and Their Polymerization

Vinyl ethers(VE) possess double bond with high electron densities due to their strong electron-donating alkoxy substituent.[55] The general molecular structure of vinyl ethers is depicted in Figure 2.19.

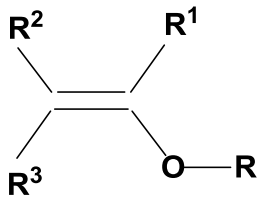
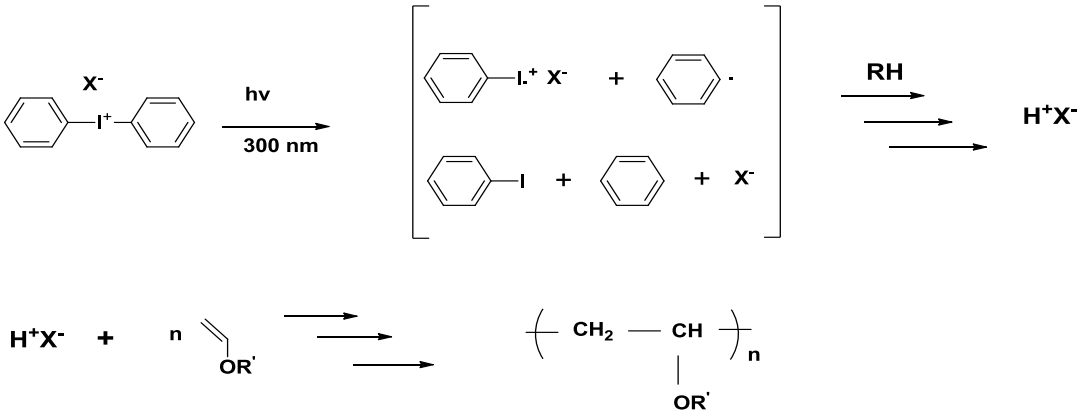


Figure 2.19 The chemical structure of vinyl ether.

VEs attract interest due particularly to its predominant role in the photopolymerization. Many researches have been performed and still continues with respect to the photopolymerization of vinyl ethers. Vinyl ethers can be used as a monomer either by free radical photopolymerization or cationic photopolymerization. Even though the majority of industrial applications are based on free radical photopolymerization, the corresponding cationic mode is also VEs attract interest due particularly to its predominant role in the photopolymerization. Many researches have been performed and still continues with respect to the photopolymerization of vinyl ethers. Vinyl ethers can be used as a monomer either by free radical photopolymerization or cationic photopolymerization. Even though the majority of industrial applications are based on free radical photopolymerization, the corresponding cationic mode is also important industrial process due to its excellent benefits such as minimizing the energy consumption and eliminating the need for solvents as diluents.

Vinyl ethers are very reactive monomers that undergo a rapid cationic photopolymerization. The cationic photopolymerization of vinyl ethers with Lewis and protonic acids is know for a long time. Wislicenius already reported in 1878 that a viscous material was formed by treatment of ethoxyethene with iodine.[56] Schildknecht et al. Synthesized in 1947 poly(1-isobutoxy-ethylene) by treatment of isobutoxyethene with BF_3 and BF_3. ET_2O. [57]Later, vinyl ethers were also polymerized with protonic acids[58] such as halogenated metalalkanes,[59] Ziegler-Natta catalysts and carbocations.[60] The photoinduced cationic photopolymerization of different vinyl ethers with iodonium and sulfonium salts was investigated by Crivello et al [61].

Especially, for UV-curing coatings as vinyl ethers offer environment-friendly formulations that are alternatives to commonly used acrylate monomers which possess strong odor and skin irridating properties. The classical way to initiate UV-radiation curing or cross-linking of vinyl ether monomers is based on the use of Bronsted acids that are photochemically generated from onium salts including diphenyliodonium compounds that contain metal salts such as AsF_6^-, SbF_6^-, PF_6^- as a counter anion as can be seen in Figure 2.20. One of the divergent feature of cationic UV-curing is that the chain reaction continues to proceed even in the dark, thereby achieving a more decisive deep-through cure of the sample. These low-odor and non-irritating monomers are now commercially existent, thus allowing a fine tuning the UV-curable formulation in order to attain the desired features of the polymer material for the industrial applications. UV-curable VE monomers are anticipated to find their main industrial applications including fast-drying coatings, quick-setting adhesives, sealants, negative photoresists in the graphic arts and microelectronics.



RH:Solvent or monomer
X: PF_6^- , SbF_6^- , AsF_6^-

Figure 2.20 Cationic photopolymerization of highly reactive vinyl ethers.

In addition, onium salts can be photochemically activated over a broad wavelength range with the aid of various sensitizers and free radical photoinitiators. In direct initiation iodonium salts directly absorb incident light around 300 nm and undergo decomposition to generate active species capable of initiating cationic photopolymerization of vinyl ethers. In the indirect initiation, however the light at higher wavelength is mainly absorbed by free radical photoinitiators or photosensitizers and initiating species are formed by various electron transfer reactions. Both direct and indirect systems are efficiently applied for UV-curing of vinyl ether based formulations.

2.3. Side Chain Functional Polymers

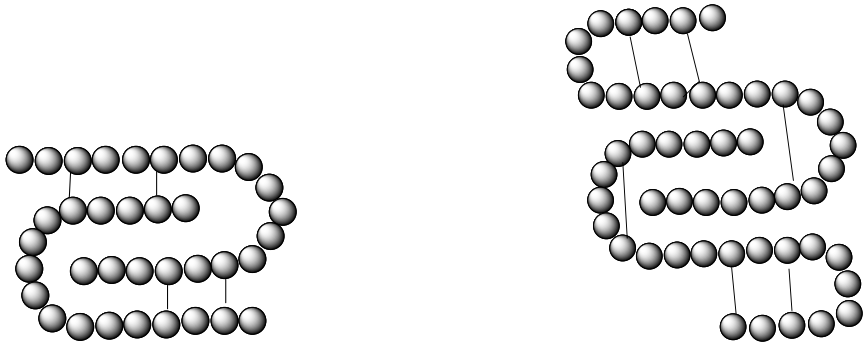
Polymers play a predominant role in the emergence of the modern world. They touch every aspect of our lives. Improvements in polymer chemistry are substantially important because it holds considerable promise in the future. There is increasing interest in preparing the polymers with various side chain functional groups and well-defined structures. There are two main approaches: construction of new molecules that are likely, from their molecular composition, to have the desired properties and modification of properties of existing large scale polymers. Modification of the polymer is essential to meet various challenges, as it is very difficult to get new polymers.

Polymer modification is essential not only to bring spesific properties to the modified material including improved thermal stability, flexibility, rigidity but also enhance

the ability to tune the functionalities and properties through chemical design. The prime techniques for polymer modifi cations are grafting, crosslinking, which are all multicomponent polymer systems [62].

The "c*rosslinking* " is the association of polymers with functionality through a chemical bond [63]. Crosslinking may occur either through the polymerization of monomers with functionality greater than 2 (by condensation mode) or by covalent bonding between preformed polymer molecules accomplished by irradiation, sulfur vulcanization, or miscellaneous chemical reactions. Crosslinking restricts chains from sliding past one another and generates elasticity in an amorphous polymer. It makes a polymer more resistant to heat, light, and other physical agencies, giving it a high degree of dimensional stability, mechanical strength, chemical and solvent resistance.

In this thesis, we have focused on ''*photocrosslinking*''. The term ''*photocrosslinking of polymer''* is defined as the process whereby light (UV, visible, or laser light) is used to induce the crosslinking of preexisting high polymers [64]. ''*Photocrosslinkable polymers''* possess functional groups which can undergo light-induced reactions to form a crosslinked polymer directly. It constitutes the basis of a considerable number of commercial applications, not only in conventional areas of thin layer materials, such as coatings, inks, photoresists, adhesives, photoimaging, and photolithography, but also in new domains using photocrosslinked polymeric materials in thick layers, such as insulating materials on wire and cable, hot water pipe, shrinkage tube and hose, and foams.



I **II**

Figure 2.21 Schema of (**I**) intermolecular and (**II**) intramolecular crosslinking.

Grafting is defined as the covalent attachment process and irreversible. Graft copolymers can be obtained with three general methods:'' *grafting-onto''*, in which side chains are preformed, and then attached to the backbone, ''grafting-from'', in which the monomer is grafted from the backbone and *''grafting-through''*, in which the macromonomers are copolymerized.

2.3.1. Grafting onto method

Grafting onto methods involve reaction of functional groups (Y) located at the chain ends of one kind of polymer with other side chain functional groups (X), which are distributed randomly on the main chain of the other polymer (Figure 2.20). The method is most suited for the reaction of "living" anionic and cationic polymers with electrophilic and nucleophilic side chain functions carried by a polymer backbone, respectively.

To give a spesific instance, the preparation of poly(butadiene-gstyrene) and poly(butadiene-g-styrene) copolymers, where the PBd backbone is synthesized by anionic polymerization, followed by introduction of chlorosilane groups, via postpolymerization hydrosilylation, and, finally, linking with living polystyrene anions [65].

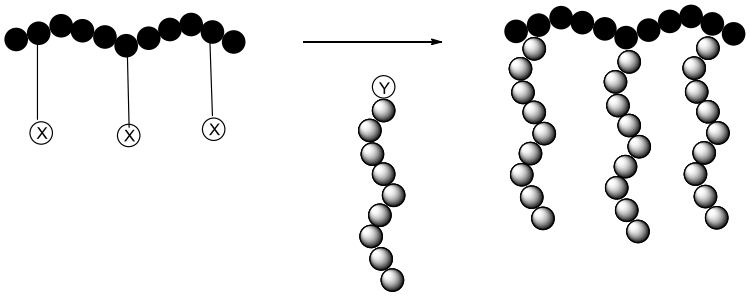


Figure 2.22 Synthesis of graft copolymer by "*grafting onto*" method.

2.3.2.Grafting from method

In this method after the preparation of the backbone, active sites are produced along the main chain, which are able to polymerize the monomer(s) that will comprise the branches. Following ''*grafting from''technic* several graft copolymers can be synthesized by the use of a number of different polymerization modes because

radicals, anions, cations can be generated along a polymer chain [66-68]. This method has found a number of applications to modify the properties of the polymers for special uses such as surface modification. In this case, a polymer backbone contains some thermally cleavable bonds such as azo and peroxide linkages (Figure 2.21). If the polymers are heated in the presence of a second monomer, initiation takes place. In such systems, homopolymer formation is unavoidable because of the concomitant formation of low molar mass radicals. For instance, side chain polymeric photoinitiators are also suitable precursors for this type of graft copolymerization.

The new advances in the living (controlled) radical polymerization techniques led to the preparation of well-defined graft copolymers. A typical example is the use of chloromethylated polystyrene, produced by controlled radical copolymerization of styrene and chloromethylstyrene, as a multifunctional ATRP initiator for the formation of graft copolymers with polystyrene backbones and branches comprised of different (meth)acrylate monomers.

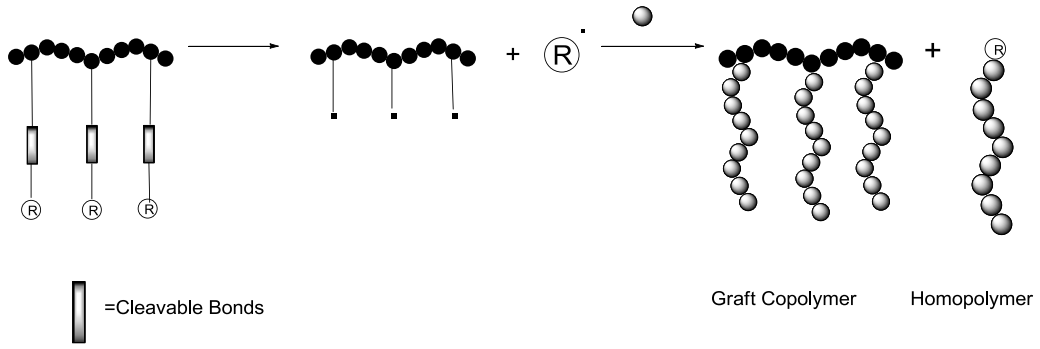


Figure 2.23 Synthesis of graft copolymer by "grafting from" method.

2.3.3 Grafting through method

Macromonomers are short polymer chains possessing a polymerizable group at one terminus. A great variety of methods involving living polymerization techniques, chain transfer reactions, and end chain modifications have been developed to synthesize such species.

In this case the macromonomer comprises the branch of the copolymer, and the backbone is formed in situ. The number of branches per backbone can be generally controlled by the ratio of the molar concentrations of the macromonomer and the

comonomer. Several other factors have to be considered. Among them the most important one is the copolymerization behavior of the macromonomer and the comonomer forming the backbone. Depending on the reactivity ratios, r1 and r2, of the reacting species, different degrees of randomness can be achieved, with respect to the placement of the branches. Because macromonomer and comonomer incorporation in the graft copolymer can vary in the course of the copolymerization reaction due to changes in the concentration of the two compounds in the mixture, different kinds of graft copolymers are formed as a function of time. Phase separation can also occur in these systems due to the formation of the copolymers, leading to increased compositional and molecular weight heterogeneity of the final product. Polystyren macromonomer formation by anionic polymerization and its subsequent use for graft copolymer with polymethyl methacrylate backbone is an example of the use of macromonomers in the synthesis graft copolymers.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

CM352a and CM92a were synthesized from Prof. H. Frey laboratory as described below. N,N-Di(p-methoxy-benzyl)-2-amino ethanol was dissolved in benzene in a 250 mL-Schlenk flask, and 0.9 equiv of cesium hydroxide were added. The mixture was stirred under argon for 3 h at room temperature and evacuated at (10_2 mbar) for 12 h to remove benzene and water, forming the corresponding cesium alkoxide. Then 20 mL of dry THF was cryo-transferred into the Schlenk flask to dissolve the initiator-salt. Ethylenoxide (EO) was first cryo-transferred to a graduated ampule, and subsequently cryo-transferred into the flask containing the initiator in THF (at around _80 _C). The ethoxy vinyl glycidyl ether (EVGE) comonomer was added via syringe and the mixture was heated to 90 ^{0}C and stirred for 24_72 h. Precipitation in cold diethyl ether resulted in the pure copolymers. For polymers with a high fraction of EVGE, the polymer solution was dried in vacuo.

4-Hydroxybutyl vinylether (HBVE, %98, BASF) was used as purchased.

Dimethyl sulfoxide (DMSO, %99.5, Aldrich) was used as purchased.

Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, %98, Alfa Aesar) was used as purchased.

Bis(2,4,6-trimethylbenzoyl)-phenyl phospine oxide (BAPO, Ciba) was used as purchased.

Camphorquinone (CQ, Ciba) was used as purchased.

3.2 The Preparation of Formulation

Mainly, formulations were prepared in order to investigate the influence of the diversified components in the photopolymerization. Typical formulation was prepared in the form of CM352a (wt. %80), DMSO (wt. %20) and $Ph_2I^+PF_6^-$ (wt. %4).

3.3 Equipments

3.3.1 Real-time infrared spectroscopy (RT-IR)

FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum One B spectrometer. The UV-radiation from a high pressure mercury arc lamp was introduced by a flexible optical fiber. The end of the optical fiber was positioned at a distance of 5 cm from the KBr disc to ensure the whole disc was irradiated by the UV light. Measurements were performed in the varied intensity of the light which applied by a UV radiometer covering broad UV range in the presence of air.

The spectra were recorded with a certain time resolution and with a spectral resolution of 4 cm^{-1} (vinyl ether double bonds). The curing reaction was followed by monitoring the decay of the intensity of the peaks at 1620 cm^{-1} by integrating the peak areas.

3.3.2 Photocalorimetry (Photo-DSC)

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a high pressure mercury arc lamp. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured by a UV radiometer covering broad UV range. The mass of the samples was 3-5 mg and the measurements were carried out in an isothermal mode at 30 $^{\circ}C$ under a nitrogen flow of 20 mL min^{-1}. The reaction heat liberated in the polymerization was directly proportional to the vinyl ether double bonds which react in the system. By integrating the area under the exothermic peak, the conversion of the vinyl ether groups (C) or the extent of the reaction was determined according to equation 3.1:

$$C = \Delta H_t / \Delta H_0^{theory} \qquad \textbf{(3.1)}$$

Where ΔH_t is the reaction heat evolved at time T and ΔH_0^{theory} is the theoretical heat for complete conversion. $\Delta H_0^{theory} = 60$ kJ mol^{-1} for an vinyl

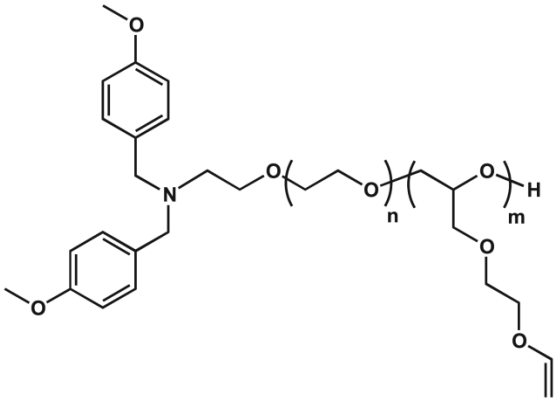
ether double bond. The rate of polymerization (Rp) is directly related to the heat flow (dH/ dT) by equation 3.2:

$$R_p = dC / dt = (dH / dt) / \Delta H_0^{theory} \quad \textbf{(3.2)}$$

4. RESULTS AND DISCUSSION

The crosslinking of vinyl ethers provide on the use of Brønsted acids photochemically generated from onium salts such as diphenyliodonium compounds with a counter anion including PF_6^-, SbF_6^-, AsF_6^- or BF_4^- in cationic photopolymerizations through direct systems [69]. Iodonium salts absorb the light about 300 nm and generate active species to initiate the cationic polymerization. In order to reach the accuracy of yield, the indirect systems can be applied by using free radical photoinitiators and photosensitizers that absorb the light at higher wavelength [70-73].

In this work, PEG copolymers which contain up to %25 vinyl ether side chains were synthesized. The overall shape and behaviours of CM352a and CM92a polymers were given in Figure 4.1 and were synthesized as described in the literature.



CM92a: n= 217, m= 14, M_n= 1700
CM352a: n= 52, m= 7, M_n= 5030

Figure 4.1 The structure of PEG-based polymers with vinyl ether side chains.

The crosslinking of PEG-based polymers with highly reactive vinyl ether side chains were investigated upon UV-irradiation in the presence of diphenyliodonium salt by means of photo-differential scanning calorimetry (Photo-DSC) and real-time infrared (RT-IR) experiments. The influence of the components in the polymerization were examined by shuffling the amount and type of the components such as solvents, applied initiating modes.

Mainly, formulations were prepared in order to investigate the influence of the diversified componets to crosslinking of PEG-based polymers with highly reactive vinyl ether side chains. Typical formulation was prepared in the form of CM352a (wt. %80), DMSO (wt. %20) $Ph_2I^+PF_6^-$ (wt. %4). The occuring reaction is depicted in Figure 4.2.

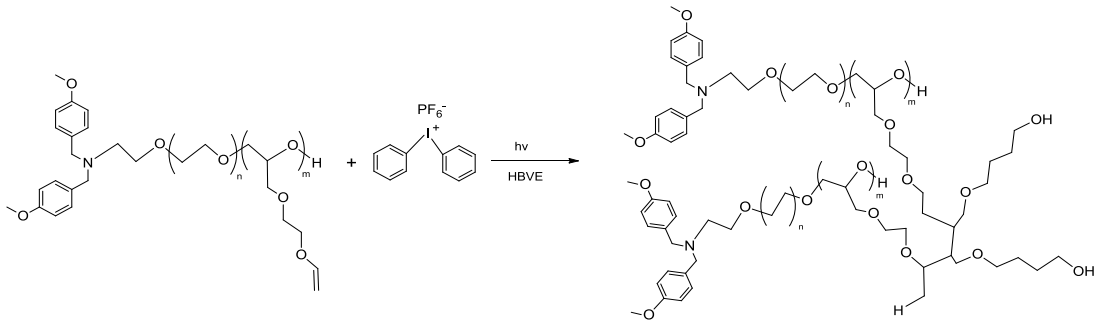


Figure 4.2 Cross-linking reaction of PEG-Based Polymer withVinyl Ether Side.

4.1. Effect of the Solvent

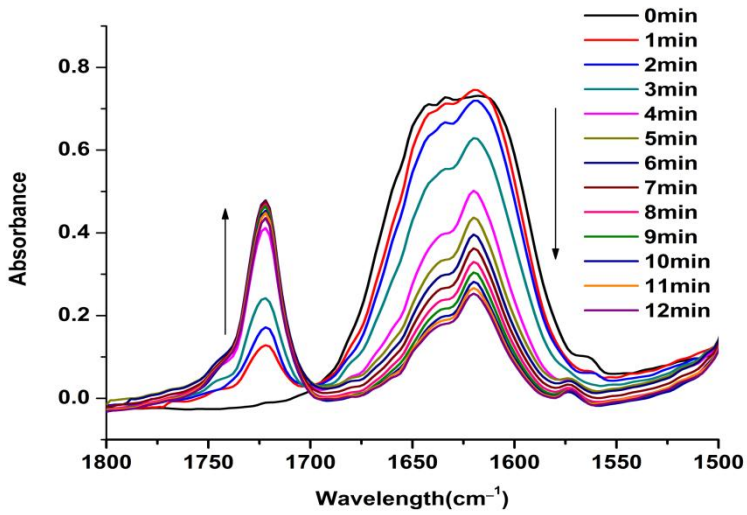


Figure 4.3 The IR absorbance change of the vinyl group during ET-5(80 wt% CM352a-20 wt% DMSO) photopolymerization in the presence of $Ph_2I^+PF_6^-$.

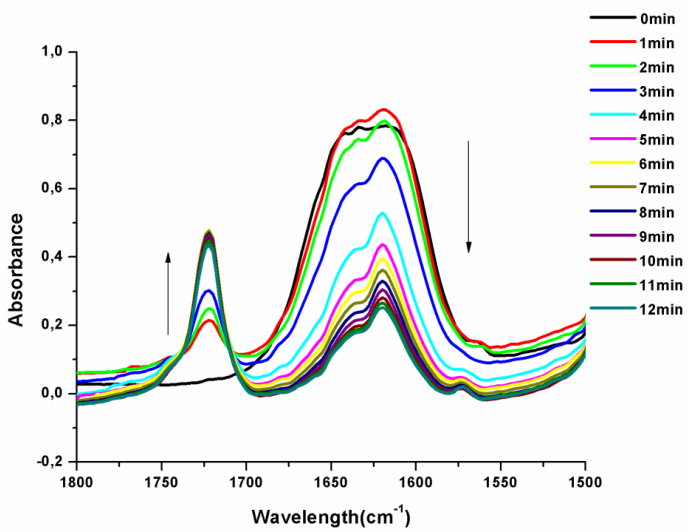


Figure 4.4 The IR absorbance change of the vinyl group during ET6(80 wt% CM352a-20 wt% HBVE) photopolymerization in the presence of $Ph_2I^+PF_6^-$.

PEG-based polymers with highly reactive vinyl ether side chains are seem to be very attractive system in UV-curing applications. Under irradiation in the presence of an diphenyliodonium hexafluorophosphate salt, the photoinduced cationic polymerization of these polymers propagate rapidly and converted to insoluble polymers [71]. When the polymers are irradiated under the UV, we have observed decrease in the vinyl ethers peak area as can be seen in Figure 4.3 and Figure 4.4.

The double bond conversion is related to the solvent of the formulation. Double bond conversion of vinyl ether group can be defined according to the equation 4.1 as shown below.

$$\% \text{ Conversion} = (A_0 - A_t / A_0) * 100 \qquad \textbf{(4.1)}$$

Where A_0 is the peak area of vinyl ethers before irradiation and A_t is the peak area of remaning vinyl ethers after the irradiation initiates during the reaction period. By using this equation, the influence of different solvents to the double bond conversion is shown in Figure 4.5.

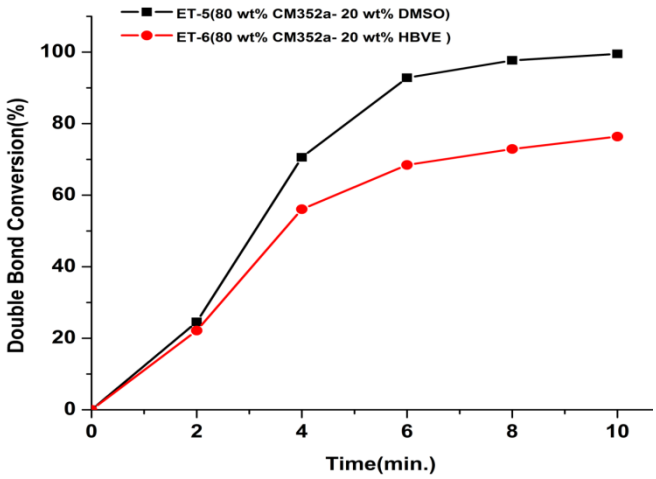


Figure 4.5 Comparison of double bond conversion of ET-5 and ET-6. $[Ph_2I^+PF_6]$=4 wt%.

The photoinduced cationic polymerization of PEG-based polymers with highly reactive vinyl ether side chains proceeds briskly to comprise a crosslinked polymer network. Hydroxy butyl vinyl ether is used not only as solvent but also it has a monomer functionality due to its vinyl ether group.

In the experimentation of ET-5, intramolecular crosslinking is observed only between the vinyl ether side chains of PEG-Based polymer. However, in the experimentation of ET-6, as well as intramolecular crosslinking, intermolecular crosslinking is obtained between the vinyl ether group of hydroxy butyl vinyl ether and vinyl ether group of PEG-Based polymer. Because of that, in the experimentation of ET-6 we have observed less conversion than ET-5. Hence, we can imply that hydroxyl butyl vinyl ether buildup a tightly cross-linked polymers with the CM352a, the polymerization terminates faster than ET-5.

4.2. Effect of the Amount of the HBVE

Resulting from the crosslinking effect of hydroxy butyl vinyl ether, the influence of the amount of hydroxy butyl vinyl ether to crosslinking was examined. Because of the monomer functionality of HBVE, when the amounts of HBVE increases, rising of the occurring cross-linking between the highly reactive vinyl ether side chains of

PEG-based polymer and the vinyl ether groups of HBVE can be seen from the Figure 4.6.

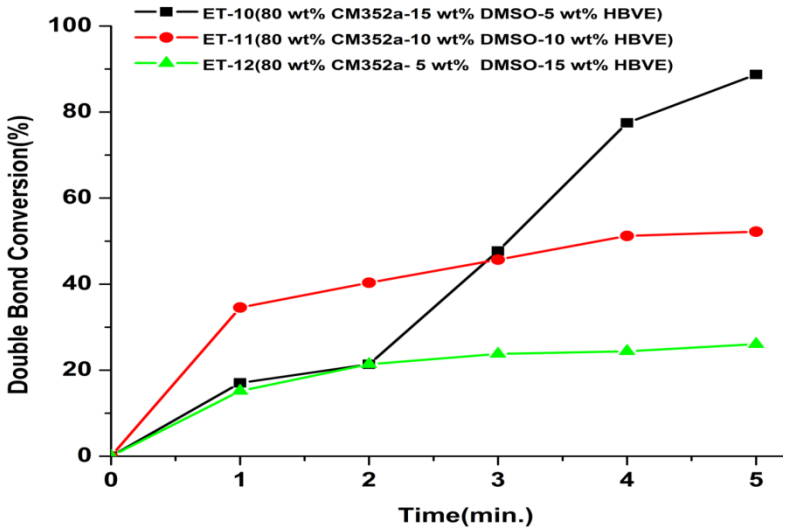


Figure 4.6 Comparison of double bond conversion of ET-10, ET-11, ET-12.[$Ph_2I^+PF_6$]= 4 wt%.

It is observed that from the experimental ET-12, which includes the maximal HBVE, the less double bond conversion is seen due to highly cross-linking tending feature of HBVE. Consequently, the concentration of the HBVE in the formulation was found to play a predominant role on both the cure speed and final conversion.

4.3. Comparison of the Initiating Mode

The cationic polymerization of vinyl ether groups were achieved upon UV irradiation of DMSO and HBVE solutions containing diphenyliodonium hexafluorophosphate. For comparison, the indirect system (free radical promoted cationic polymerization and photosensitized cationic polymerization) photoinitiators such as BAPO, camphorquinone were also applied.

Table 4.1 The Photo-curing by direct and indirect cationic polymerization modes of the PEG-based polymers with vinyl ether side chains.

Run	$Ph_2I^+PF_6^-$ [wt. %]	CQ [wt. %]	BAPO [wt. %]	Double Bond Conversion (%)
ET-21	2	2	-	16
ET-20	4	-	-	54
ET-22	2	-	2	56

CM92a/HBVE (wt. % 80/ 20) $Ph_2I^+PF_6^-$(diphenyliodonium hexafluorophosphate), CQ(camphorquinone), BAPO(bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide)

The kinetics of the cationic polymerization of VEs is basically operated by the initiation process which relate to the type of onium salt used. For diphenyliodonium salts, the overall photolysis process can be schematically represented in Figure 2.18.For comparison, free radical promoted cationic photopolymerization modes as indirect initiating systems were also applied. BAPO, which is a free radical photoinitiator, in combination with appropriate diphenyliodonium hexafluorophosphate is efficient photoinitiators for cationic polymerization. Moreover, further double bond conversion was observed in this system that can be seen from Table 4.1.

The estimated mechanism involves the photogeneration of benzoyl radicals and phosphinoyl radicals. Since the stability of phosphinoyl radicals is rather than benzoyl radicals, subsequent reaction carry on from the phosphinoyl radicals. Posterior oxidation of them by diphenyliodonium hexafluorophosphate yield phosphonium ions capable of initiating the polymerization of vinylethers. It can be schematically shown as follows in Figure 4.7 [74].

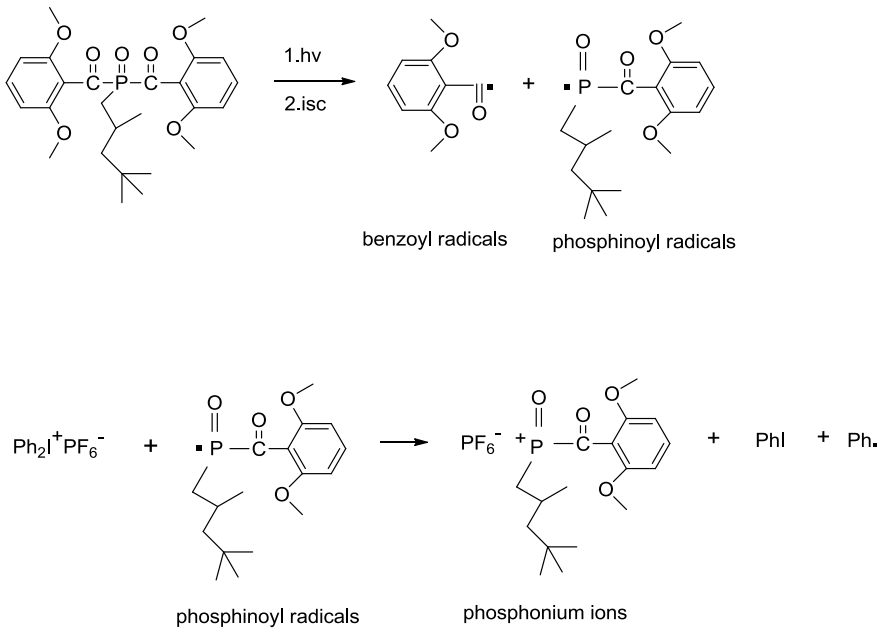


Figure 4.7 The estimated reaction mechanism between BAPO and $Ph_2I^+PF_6$.

Besides that, the compatibility of camphorquinone (CQ), which has a relatively strong absorbance in the 375-500 nm region, as a photosensitizer with $Ph_2I^+PF_6$ was examined. However, CQ/ $Ph_2I^+PF_6^-$ initiating system was not compatible with each other since the less double bond conversion was perceived. Because the CQ mechanism involves the reduction of the CQ excited state to a ketyl radical by a H donor (monomer or solvent) followed by the oxidation of the ketyl radical by the iodonium salt and thus regeneration of the CQ. This means that, this regeneration puts back the double bond conversion. It can be schematically shown in Figure 4.8 as follws [75].

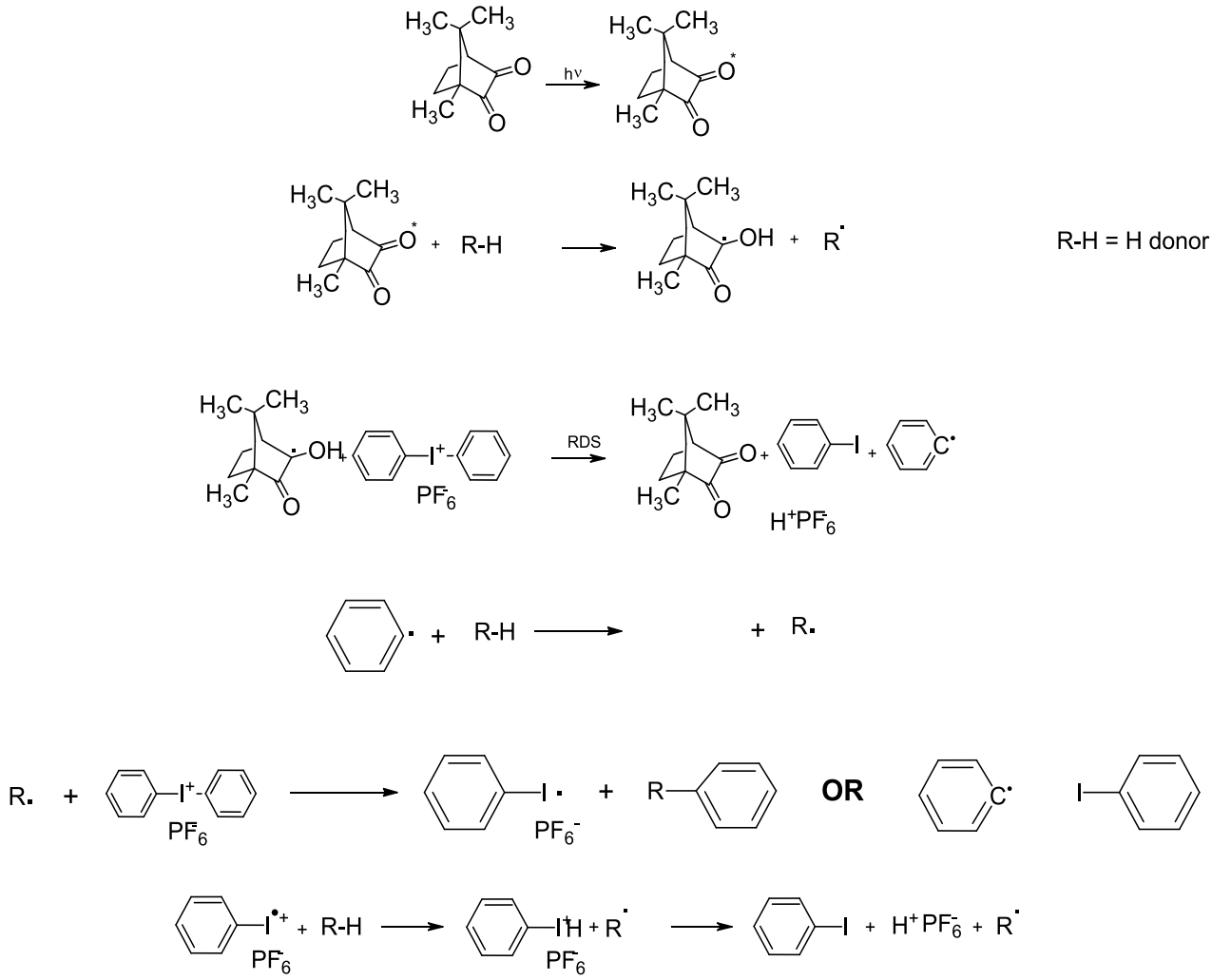


Figure 4.8 Proposed photosensitization of Ph_2IPF_6 by CQ during polymerization.

4.4. Effect of the applied Intensity

The rate of the cationic photopolymerization of VEs depend on the light intensity. In order to observe the effect of the light intensity into photopolymerization, formulations which contain different type of solvents in the presence of diphenyliodonium hexafluorophosphate were prepared and were analyzed by means of Photo-DSC experiments. The rate of polymerization and double bond conversion in the different solvents; DMSO and HBVE, respectively, can be seen from Figure 4.9, 4.10 , 4.11 , 4.12 .

By integrating the area under the exothermic peak, the conversion of the vinyl ether groups (C) or the extent of the reaction was determined according to equation 4.2:

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \qquad \textbf{(4.2)}$$

Where ΔH_t is the reaction heat evolved at time T and $\Delta H_0^{\text{theory}}$ is the theoretical heat for complete conversion. $\Delta H_0^{theory} = 60$ kJ mol^{-1} for an vinyl ether double bond. The rate of polymerization (Rp) is directly related to the heat flow (dH/ dT) by equation 4.3:

$$R_p = dC / dt = (dH / dt) / \Delta H_0^{\text{theory}} \qquad \textbf{(4.3)}$$

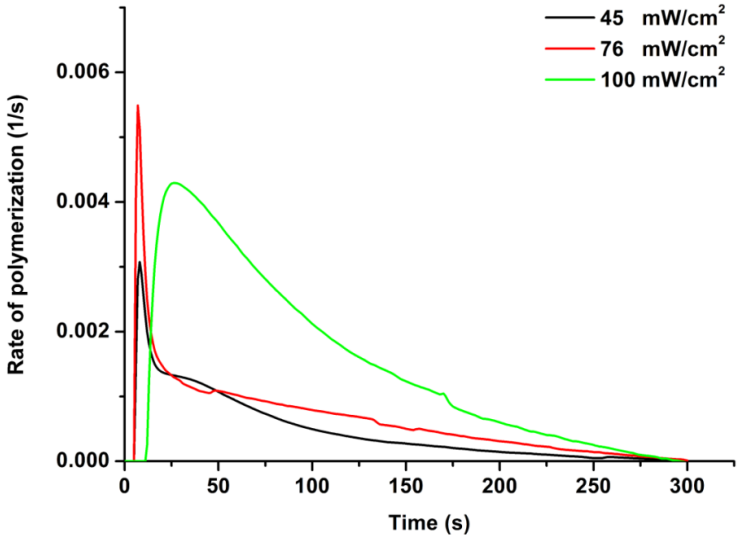


Figure 4.9 Rate of polymerization vs. time plot for the photopolymerization of CM92a initiated by 4 wt % $Ph_2I^+PF_6^-$ in DMSO solution at 30°C.

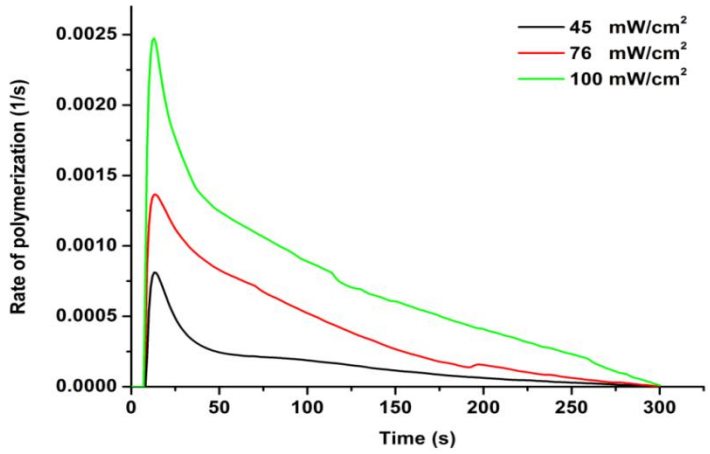


Figure 4.10 Rate of polymerization vs. time plot for the photopolymerization of CM92 initiated by 4 wt % $Ph_2I^+PF_6^-$ in HBVE solution at 30°C.

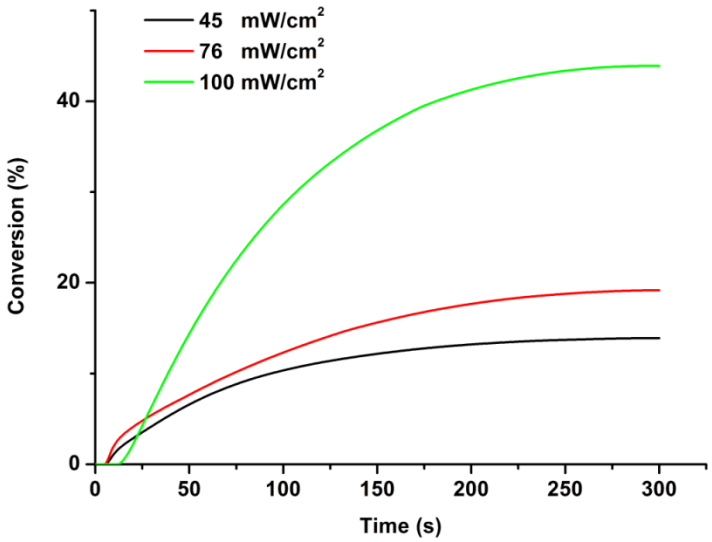


Figure 4.11 Conversion vs. time plot for the photopolymerization of CM92a initiated by 4 wt % $Ph_2I^+PF_6^-$ in DMSO solution at 30°C.

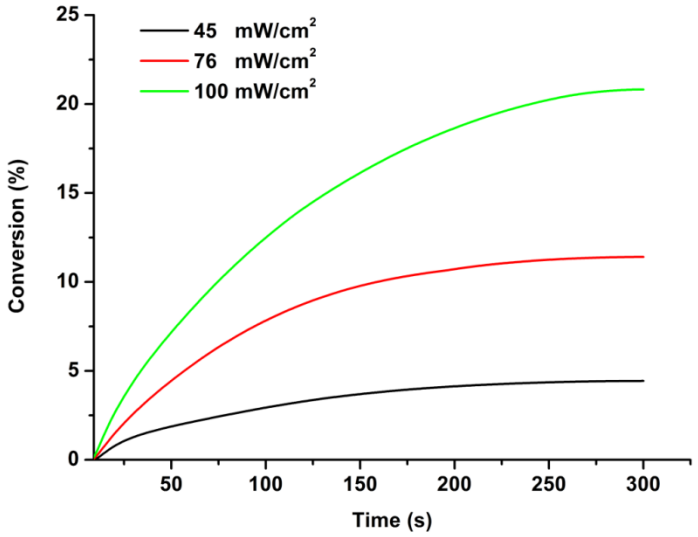


Figure 4.12 Conversion vs. time plot for the photopolymerization of CM92a initiated by 4 wt % $Ph_2I^+PF_6^-$ in HBVE solution at 30°C.

It is proved that the double bond conversion of vinyl ether groups is compatible with the increasing light intensity that can be seen from the Figure 4.11, 4.12. Double bond conversion of different formulations which contain DMSO and HBVE were arised by performing the increase of light intensity.

In addition, crosslinking effect of HBVE was proved by means of Photo-DSC as well as RT-IR experiments.

5. CONCLUSIONS AND RECOMMENDATIONS

In this thesis, the crosslinking feature of PEG-based polymers with highly reactive vinylether side chains in the presence of a solvent, dimethyl sulfoxide, and a reactive monomer, hydroxybutyl vinyl ether with diphenyliodonium hexafluorophosphate salt was investigated through photoinduced cationic polymerization. Due mainly to the monomer functionality of HBVE , it favors premature crosslinking of PEG-based polymers with highly reactive vinyl ether side chain rather than DMSO. Obviously, HBVE readily reacts with the propagating side chains in an intermolecular and intramolecular manner leading to crossling. However, DMSO is an inert molecule possesing no reactive groups in the structure. Hence, less overall double bond conversion was observed in the presence of HBVE compared to DMSO.

Furthermore, to point out differences as well as parallels between the initiators for direct and indirect action(free radical promoted cationic polymerization, photosensitized cationic polymerization). It is observed that BAPO, which is a long wavelength free radical photoinitiator, in combination with appropriate diphenyliodonium hexafluorophosphate are efficient photoinitiators of cationic polymerization. Thence, furthest double bond conversion was observed in this system. Moreover, the compatibility of camphorquinone (CQ), which has a relatively strong absorbance in the 375-500 nm region, as a photosensitizer with $Ph_2I^+PF_6$ was examined. However, CQ/ $Ph_2I^+PF_6^-$ initiating system was not compatible with each other since the less double bond conversion was perceived.

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